BNa–BLi solid-solution in A-site-vacant amphiboles: synthesis and cation ordering along the ferri-clinoferroholmquistite–riebeckite join.

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^{B}Na–^{B}Li solid-solution in A-site-vacant amphiboles: synthesis and cation ordering along the ferri-clinoferroholmquistite–riebeckite join

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ABSTRACT

Amphiboles were hydrothermally synthesized at 500 °C and 4 kbar in the system Li_2O-Na_2O-FeO-Fe_2O_3-SiO_2-H_2O, with nominal compositions along the riebeckite [$\square Na_2Fe^{2+}_3Fe^{3+}_2Si_8O_{22}(OH)_2$]-ferri-clinoferroholmquistite [$\square Li_2Fe^{2+}_3Fe^{3+}_2Si_8O_{22}(OH)_2$] join, where the exchange vector is $NaLi_{-1}$ at the B-site. Experimental products were characterized by powder XRD and SEM-EDAX, confirming very high amphibole yield along the join (>95%, plus minor quartz). The XRD patterns can be indexed in *C*2/*m*, and the refined cell parameters show linear variation as a function of composition. For the ^{B}Li end-member, the IR spectrum shows a single sharp main band centered at 3614 cm^{-1}, which is assigned to the FeFeFe-OH-$^{A}\square$ configuration. With increasing ^{B}Na in the mineral, this band broadens and shifts 4 cm^{-1} to higher frequencies. This effect can be attributed to the change in M4 site occupancy. Minor ^{A}Na (partial solid-solution toward arfvedsonite) is also observed with increasing sodium in the system. Mössbauer spectroscopy confirms the cation distribution provided by IR data, and shows that a small, but significant amount of Fe^{2+} occurs at M4 along the join. Infrared spectroscopy shows that the Li end-member has a very ordered structure, whereas intermediate compositions show local heterogeneities associated with the presence of two different B sites occupied by Na or Li.

INTRODUCTION

Li-bearing amphibole minerals belong to two main groups: Fe-Mg-Mn-Li (holmquistite) and sodic amphiboles. Holmquistite has been described from some thirty localities around the world (London 1986), whereas Li-rich sodic amphiboles have been described from igneous rocks (Questa Caldera, Hawthorne et al. 1996a; Hurricane Mountain, Hawthorne et al. 1996b; Strange Lake, Hawthorne et al. 2001), and from metamorphic rocks (Kajlidongri, India, Hawthorne et al. 1992). Both amphibole types are typical of highly fractionated syenites and alkali syenites, and granitic pegmatites (Deer et al. 1999; London 1986).

Before the 1990s, the distribution and the crystal-chemical behavior of Li in amphiboles was poorly characterized, primarily because of the difficulties in analyzing Li at the micrometer scale. These problems have been resolved with the application of micro-analytical techniques and detailed crystal-structure refinements of suites of samples from petrologically well-characterized environments. In holmquistite, $\square Li_2(Mg,Fe^{2+})_3(Al,Fe^{3+})_2Si_8O_{22}(OH)_2$, Li is a B-group cation and is completely ordered at M4. In sodic amphiboles such as leakeite, $NaNa_2[(Mg,Fe^{2+})_2(Al,Fe^{3+})_2Li]Si_8O_{22}(OH)_2$, Li is a C-group cation and is strongly ordered at M3 (Hawthorne et al. 1993, 1994).

Sodic ferripedrizite, $Na(Na,Li)_2[(Mg,Fe^{2+})_2(Al,Fe^{3+})_2Li]Si_8O_{22}(OH)_2$ (Oberti et al. 2000; Caballero et al. 2002), has Li at both the M4 and M3 sites, thus bridging the Mg-Fe-Mn-Li and the Na amphibole groups.

The available data show that Li can enter the amphibole structure through two main exchange reactions: (1) 2 $^{[M2,3]}(Fe^{2+}, Mg) = {}^{[M3]}Li + {}^{[M2]}(Fe^{3+}, Al)$, connecting arfvedsonite (eckermannite) with leakeite (Hawthorne et al. 1994); and (2) $^{[M4]}Na = {}^{[M4]}Li$, connecting riebeckite with clinoholmquistite and leakeite with pedrizite (Oberti et al. 2000). The apparent exchange vector $^{A}Na + {}^{[M3]}Li = {}^{A}\square + {}^{[M3]}Mg$ is the sum of different mechanisms and has no crystal-chemical significance, as it does not allow for local charge balance (Caballero et al. 2002; Oberti et al. 2003).

Holmquistite and riebeckite are classified in two different groups (Leake et al. 1997) and it has been assumed that there is a miscibility gap between these two amphiboles (Deer et al. 1999). However, recent investigation of amphiboles from the Pedriza Massif, Sierra de Guadarrama, Spain (Caballero et al. 1998; Oberti et al. 2000; Caballero et al. 2001) showed complete miscibility between Na and Li at the B-group sites (Caballero et al. 2002; Oberti et al. 2003).

There are no experimental studies concerning the relation

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between Na-rich and Li-rich amphiboles. End-member riebeckite [$\square Na_2Fe^{2+}_3Fe^{3+}_2Si_8O_{22}(OH)_2$] was synthesized by Ernst (1962) who also studied its stability as a function of T, P, and f_{O_2}. Here, we present a crystal-chemical characterization of synthetic riebeckite, and show that complete exchange between Na and Li at the B-site in the amphibole structure can occur at relatively low T and P.

EXPERIMENTAL METHODS

Starting materials were prepared as silicate gels according to the method of Hamilton and Henderson (1968). Intermediate compositions were prepared by mixing end-member gels in stoichiometric proportions at intervals of 20 mol%. The starting materials were placed in gold capsules, together with 15 wt% bi-distilled water, and the capsules were then arc-welded. Hydrothermal syntheses were done using internally heated pressure vessels at T = 500 °C and P_{H_2O} = 4 kbars for a duration of 14 days. The f_{O_2} is considered as internally buffered for all experiments, as the permeability of gold is very low at this temperature (Chou 1987; Iezzi et al. 2003). The temperature was monitored by three sheathed type-K thermocouples closely adjoining the sample position (accuracy ±5 °C). Pressure was continuously recorded by a strain gauge, calibrated against a Heise-Bourdon tube gauge (error = ±20 MPa, Scaillet and Evans 1999). The experiments were quenched by switching off the current supply, thus causing a temperature drop of about 40 °C/min down to ambient temperature.

Step-scan X-ray powder-patterns were collected on a Scintag X1 diffractometer, operating in the vertical θ-θ configuration, with Ni-filtered Cu$K\alpha$ radiation and a Si(Li) solid-state detector. Cell dimensions were refined by whole-powder-pattern refinement (Rietveld method) using DBW3.2 (Wiles and Young 1981). Samples were prepared for FTIR spectroscopy as KBr pellets using the procedure of Robert et al. (1989a). FTIR spectra in the OH-stretching region (4000–3000 cm^{-1}) were collected at room temperature with a Nicolet 760 spectrophotometer equipped with a DTGS detector and a KBr beamsplitter. Nominal resolution was 2 cm^{-1}, and the spectra are the average of 64 scans. The relative changes in line width of the absorption profiles were quantified by the autocorrelation function, following the method described in Salje et al. (2000). Mössbauer spectra were recorded in transmission mode at 297 K, with a conventional constant-acceleration Mössbauer spectrometer. The source was ^{57}Co/Rh with an activity of about 370 MBq (10 mCi). Calibration was done using either an α-Fe foil or an SNP absorber. Isomer shifts are expressed relative to α-Fe; doublets were fitted with unconstrained parameters. Additional details of sample preparation and experimental conditions can be found in Iezzi et al. (2003).

EXPERIMENTAL RESULTS

The synthesis products were characterized by powder XRD and by optical and electron microscopy. The powders consisted primarily of amphibole, with minor quartz; for all experiments the amphibole yield is considered to be >95%. The amphibole crystals (Fig. 1) are acicular, with average dimensions of 1 to 5 μm length and 0.2–1 μm width. The small size of the amphibole crystals precluded EMPA analysis.

Cell parameters

All XRD patterns were indexed in $C2/m$. The a edge, the β angle, and V decrease linearly as Li increases (Na decreases) at the B-site (Table 1, Fig. 2), whereas the b and c dimensions remain virtually constant.

The variation in β agrees very well with the data of Oberti and Ghose (1993) and Robert et al. (1993) on the relation between the aggregate cation radius at the B-site and β angle. In particular, the data presented here confirm the different trends for monovalent and divalent substitutions at M4 predicted by Oberti and Ghose (1993, see Fig. 3). Figure 3 shows that cation charge is the principal factor in controlling the slope of the trend. However, other factors also play a role; for example, the nature of the A-cation significantly affects the position of the regression line, as indicated by the parallel trends observed for ^{B}Sr substituted richterites (Fig. 3).

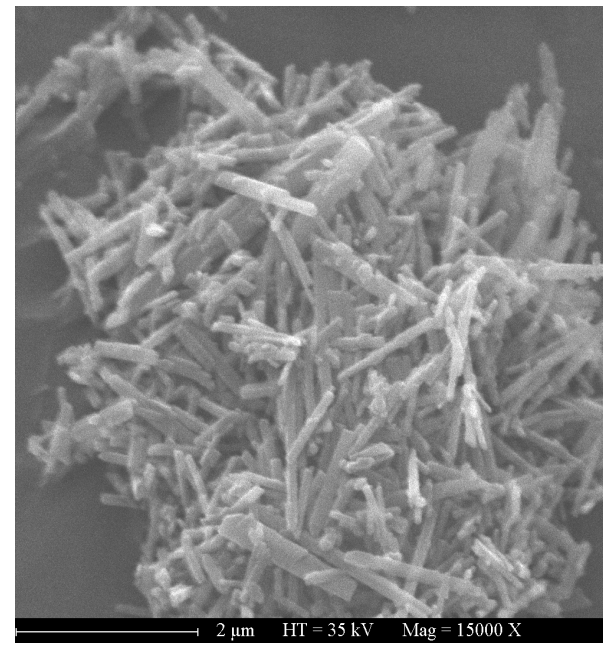

FIGURE 1. SEM image of synthetic end-member riebeckite (sample 237). The scale bar is 2 μm. The amphibole crystals are acicular and between 0.1–0.2 μm across and 0.5 to 2 μm long.

TABLE 1. Refined cell parameters along the ferro-ferriclinoholmquistite-riebeckite join

Sample	Li/(Li + Na)	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
231	100	9.512(4)	18.064(9)	5.323(2)	101.88(5)	895.22
232	80	9.555(3)	18.089(7)	5.325(1)	101.80(3)	901.77
233	60	9.612(1)	18.090(2)	5.3266(7)	102.28(1)	904.83
234	50	9.645(1)	18.090(2)	5.3267(6)	102.50(1)	906.85
235	40	9.678(1)	18.076(2)	5.3273(7)	102.76(1)	908.41
236	20	9.726(1)	18.074(2)	5.3286(6)	103.14(1)	911.89
237	0	9.773(1)	18.078(2)	5.3319(7)	103.40(1)	916.51

Mössbauer spectroscopy

Mössbauer spectra were recorded from the Li and Na end-member experimental products and from the intermediate ^{B}(LiNa) composition. The Mössbauer parameters are listed in Table 2, and the resolved spectra are stacked in Figure 4. The spectrum of end-member ferri-clinoferroholmquistite was described by Iezzi et al. (2003). It shows three well-defined doublets, two assigned to Fe^{2+} and one assigned to Fe^{3+}. On the basis of known literature data on amphiboles (Hawthorne 1983a, 1983b; Redhammer and Roth 2002), the Fe^{2+} doublet with the largest quadrupole splitting (2.82 mm/s, Table 2) was assigned to Fe^{2+} at M1, and the doublet with QS = 2.25 mm/s was assigned to Fe^{2+} at M3. The doublet with the smaller isomer shift and quadrupole splitting was assigned to Fe^{3+} at M2 (Table 2 and Fig. 4). The Fe^{2+}/Fe^{3+} ratio, calculated from the band areas for this sample, is 1.5, in agreement with the nominal compo-

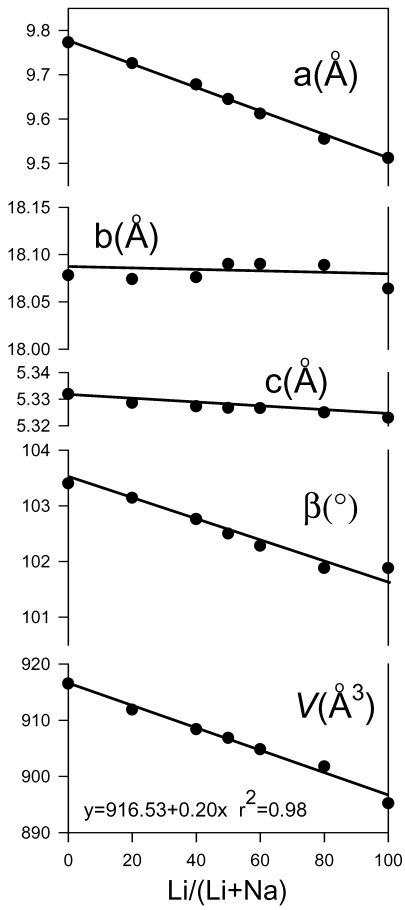

FIGURE 2. Variation in cell parameters and volume for synthetic amphiboles along the riebeckite-ferri-clinoferroholmquistite join.

TABLE 2. Mössbauer parameters for analyzed amphiboles

Sample Li/(Li + Na)	Site	Isomer shift δ (mm/s)	Quadrupole splitting Δ (mm/s)	Γ FWHH (mm/s)	/Relative site distribution (%)	χ^2
231 – Li 100	M1 Fe^{2+}	1.13(1)	2.82(1)	0.29(1)	38	1.15
	M3 Fe^{2+}	1.11(1)	2.25(1)	0.33(1)	21	
	M2 Fe^{3+}	0.39(1)	0.28(1)	0.32(1)	41	
234 – Li 50	M1 Fe^{2+}	1.15(1)	2.82(1)	0.32(1)	38	1.91
	M3 Fe^{2+}	1.08(1)	2.43(1)	0.45(1)	20	
	M2 Fe^{3+}	0.39(1)	0.34(1)	0.37(1)	38	
	M4 Fe^{2+}	1.10(1)	1.80(1)	0.37(1)	4	
237 – Li 0	M1 Fe^{2+}	1.14(1)	2.85(1)	0.33(1)	41	1.07
	M3 Fe^{2+}	1.10(1)	2.40(1)	0.30(1)	15	
	M2 Fe^{3+}	0.44(1)	0.39(1)	0.37(1)	40	
	M4 Fe^{2+}	1.80(1)	1.10(1)	0.32(1)	4	

sition (Iezzi et al. 2003). In the Mössbauer spectra of Na-bearing amphiboles (samples 234 and 237), there is a fourth less-intense doublet (Table 2 and Fig. 4) that can be assigned to Fe^{2+} at M4 (Hawthorne 1983a; Redhammer and Roth 2002), suggesting a slight departure from nominal stoichiometry (this was also confirmed by IR spectroscopy, see below). For Na-bearing samples, Fe^{2+}/Fe^{3+} is reasonably close to the nominal value (1.5). The resolved doublets in end-member ferri-clinoferroholmquistite are significantly sharper (except that of sample 237, assigned to M3) than those in the Na-rich compositions (Table 2 and Fig. 4). According to Hawthorne (1983a,

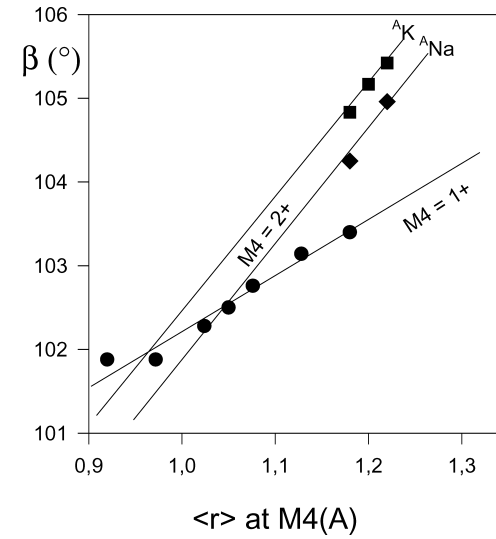

FIGURE 3. Relation between β and the mean ionic radius at M4 for some synthetic amphiboles. Circles = this work; squares = ^{B}Sr substituted potassium-richterite, diamonds = ^{B}Sr substituted sodium-richterite; data from Robert et al. (1993).

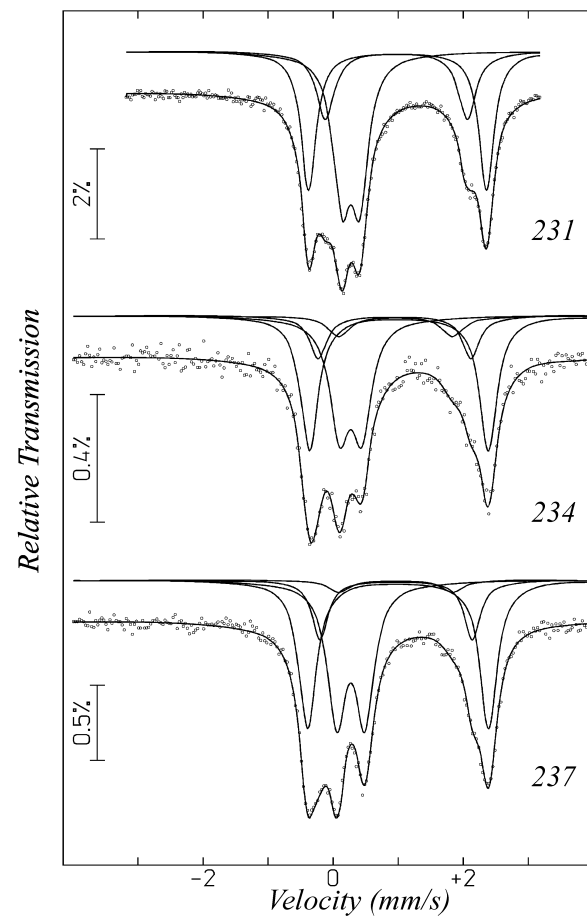

FIGURE 4. Mössbauer spectra of the two end-members and the 50:50 composition along the ferri-clinoferroholmquistite-riebeckite join.

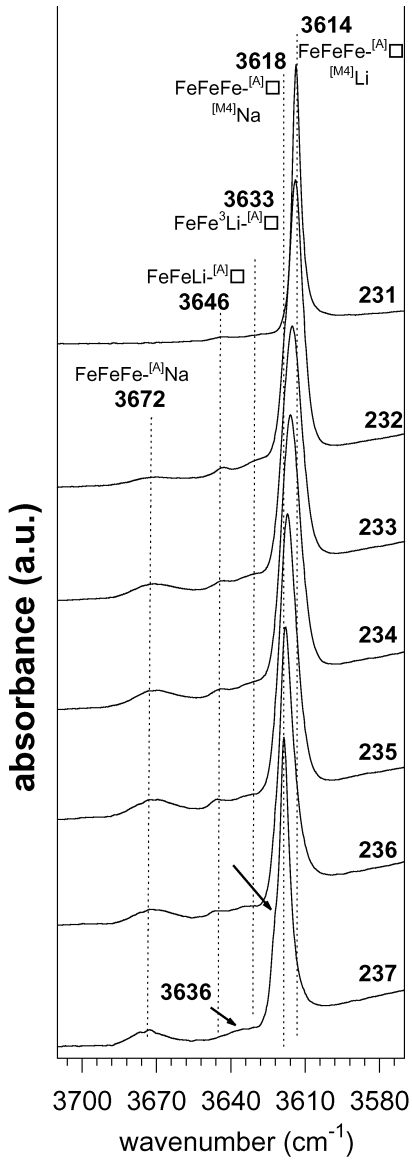

FIGURE 5. Infrared spectra in the OH-stretching region for synthetic amphiboles along the ferri-clinoferroholmquistite-riebeckite join. For the unlabeled arrow see text.

1983b), the broadening of the Mössbauer doublets is consistent with increasing disorder at the NNN (next-nearest-neighbor) sites around Fe.

FTIR OH-stretching spectra

All IR spectra in the OH-stretching region are very similar, and are dominated by one main band (Fig. 5). In end-member ferri-clinoferroholmquistite (sample 231, Fig. 5), this band is very sharp (FWHM 4 cm^{-1}), roughly symmetric, and is centered at 3614 cm^{-1}. With increasing ^{B}Na, this band broadens and shifts linearly toward higher frequency. In end-member riebeckite (sample 237, Fig. 5), it is centered at 3618 cm^{-1} and is asymmetric toward the high-frequency side, suggesting the presence of a second overlapping component at 3620 cm^{-1} (marked by an arrow in Fig. 5). The IR spectra in the OH-stretching region also show other minor features that represent less than 5% of the total absorbance. The most prominent feature is a broad band centered at 3672 cm^{-1} in end-member riebeckite. This band appears with introduction of Na into the system; its intensity increases slightly with increasing Na, up to X_{Na} (where X_{Na} = Na/Na + Li) = 0.40, and then remains roughly constant up to X_{Na} = 1 (Fig. 5). In addition, the position of this band shifts toward higher frequency with increasing Na. A second minor feature occurs at 3646 cm^{-1}, but is not present in end-member riebeckite (Fig. 5). A third minor feature occurs at 3636 cm^{-1}; it is barely discernable in the spectrum of end-member Na-free ferri-clinoferroholmquistite, and increases slightly in intensity with increasing Na.

Assignment of the FTIR bands

Assignment of the several components in the spectra of Figure 5 is based on previous work on amphiboles (e.g., Della Ventura 1992; Della Ventura et al. 1997, 1999). The basic assumption is that any charge-balance perturbation at both the NN (nearest-neighbor) and NNN local environments around the O3 anion causes a wavenumber shift of the OH-stretching band with respect to a reference band. The reference band in this system is obviously the main peak at 3614–3618 cm^{-1}; this band is assigned to the $^{[M1]}Fe^{2+[M1]}Fe^{2+[M3]}Fe^{2+}$-OH-^{A}□-^{B}Li configuration (Iezzi et al. 2003). Note that in all samples the intensity of this band is >95% of the total absorbance, indicating that Fe^{2+} is almost the only occupant of the M1 and M3 sites that bonds to OH at O3; this observation, coupled with the Mössbauer data for the same samples, indicates that the long-range composition of these amphiboles is very close to the nominal value.

The occupancy of the A-site in amphiboles has a major effect on the OH-spectrum; this feature was firstly recognized by Rowbotham and Farmer (1973), and was later characterized by Robert et al. (1989a), Della Ventura (1992), and Hawthorne et al. (1997), among others. In an A-site occupied amphibole, the OH-band is ~ 60 cm^{-1} higher than in an A-site vacant amphibole with an identical NN local environment around O3. The frequency of the broad band at ~3672 cm^{-1} is 60 cm^{-1} higher than that of the main peak at 3614–3618 cm^{-1}, and hence this band can be confidently assigned to the configuration $^{[M1]}Fe^{2+[M1]}Fe^{2+[M3]}Fe^{2+}$-OH-^{A}Na-^{B}LiNa; it indicates the presence of a small amount of Na at the A-site. This assignment is also consistent with the fact that this band appears in the IR spectrum as Na is added to the system.

The first spectroscopic (IR) evidence of ^{C}Li in amphiboles was given by Addison and White (1968) who reported the presence of a band due to the MgMgLi-OH configuration in the spectrum of a natural Li-bearing riebeckite. This band was shifted to higher frequency with respect to the MgMgMg-OH band; however, the exact frequency was not given. From the work of Robert et al. (1989b) on synthetic micas, we know that the presence of a monovalent cation (Li) at the octahedral sites causes a wavenumber shift of +30 cm^{-1} of the OH-band, due to the +5 aggregate cation charge (MgMgLi) at the NN octahedral environment around the OH group. The minor band at 3646 cm^{-1} is shifted 30 cm^{-1} toward higher frequency

with respect to the main band at 3614 cm^{-1}; therefore, it can be assigned to the configuration $^{[M1]}Fe^{2+[M1]}Fe^{2+[M3]}$Li-OH-$^{A}\square$. Note that this band in not present in the spectrum of end-member riebeckite. Its presence in all spectra along the join suggests that a very small amount of Li enters the octahedral strip in all of the amphibole samples. Single-crystal structural work on amphiboles shows that ^{C}Li is strongly ordered at M3 (Hawthorne et al. 1994; Oberti et al. 2003).

Finally, assignment of the minor band at 3633 cm^{-1} is difficult. On the basis of the data discussed above, it must be assigned to a configuration with a vacant A-site. Given the chemical system, we are left with the configuration $Fe^{2+}Fe^{3+}$Li-OH-$^{A}\square$. This inference is supported by the work of Della Ventura et al. (1999) on synthetic pargasite-richterite solid-solutions, which shows that the presence of a trivalent cation (Al) at the NN OH-coordinated sites produces a negative shift of ~15 cm^{-1}; actually, the 3633 cm^{-1} band is shifted 13 cm^{-1} with respect to the $Fe^{2+}Fe^{2+}$Li-OH-$^{A}\square$ band at 3646 cm^{-1}. Note that this 3633 cm^{-1} component is not present in the spectrum of end-member riebeckite (sample 237, Fig. 5), where it is replaced by a new weak band at ~3636 cm^{-1} (indicated by an unlabeled arrow in Fig. 5) whose assignment is uncertain, but is probably related to Fe^{2+} at M2.

Ordering of cations along the join

Infrared spectroscopy is extremely sensitive to both LRO and SRO, and two different methods have been developed in the last few years to characterize cation order in mineral structures. The first is based on the measure of frequencies and relative intensities of OH-stretching bands in well-characterized solid-solutions (e.g., Hawthorne et al. 1997, 2000; Della Ventura et al. 1997, 1999). However, quantitative use of this method is greatly inhibited by the ignorance of possible variation in absorption coefficients with frequency (e.g., Skogby and Rossman 1991), as discussed by Hawthorne et al. (1997). The second approach is based on the fact that vibrational spectra can show substantial line broadening and shifting as cations are substituted in a solid-solution. The line broadening is due to the local heterogeneity of a structure, which relaxes differently around cations with different size or charge (Salje et al. 2000). The resulting variation in line width is analyzed by the autocorrelation method (e.g., Salje et al. 2000; Carpenter and Boffa Ballaran 2001) which is a fast and easy way to quantify line-width variations in powder absorption spectra from sequences of samples of varying composition. The variation in calculated line-width, expressed as Δ_{corr}, scales with some local-order parameter, q_{od}. The interesting thing about this method is that one can ignore the assignment of absorption bands to specific structural environments, and this is certainly a great advantage when dealing with complex spectra. For this reason, it has been used in lattice (<1200 cm^{-1}) vibrational regions of different silicate minerals (e.g., Boffa Ballaran et al. 1998, 1999, 2000; Atkinson et al. 1999, and references therein).

The systematic presence of a single main band in the spectra (Fig. 5), shows that the amphiboles produced along the studied join are very close to the nominal compositions (see Iezzi et al. 2003). Minor departures can be ascribed to ^{A}Na (partial solid-solution toward arfvedsonite) and ^{C}Li. Infrared spectra show that ^{C}Li is not coupled with ^{A}Na, as both 3646 and 3633 cm^{-1} bands are locally connected with vacant A-sites (see preceding paragraph). This short-range-order information is in apparent contrast to the bond-valence calculations of Hawthorne et al. (1992) and to the single-crystal work of Oberti et al. (2003) which shows that $^{[M3]}$Li is locally strongly associated with Na at the A*m* site. However, it must be emphasized that we are dealing here with very small amounts of ^{C}Li in the structure, and perhaps the $^{[M3]}$Li – ^{A}Na relation, which is of general validity in controlling the bulk charge-balance in ^{C}Li-bearing amphiboles (Oberti et al. 2003), can be locally violated.

As previously stated, the main band in the spectrum of end-members ferri-clinoferroholmquistite and riebeckite are very sharp (Fig. 6); this suggests that these amphiboles have a strongly ordered structure (Iezzi et al. 2003). For intermediate ^{B}Na–^{B}Li compositions, this band broadens considerably (Fig. 6). This behavior is evidently due to Na-Li disorder at M4, and can be treated by means of the autocorrelation method. Autocorrelation spectra were calculated for the segment of the OH-spectra of Figure 5 which contains only the main OH-stretching band (3600–3625 cm^{-1}). The values of Δ_{corr} (Fig. 7) at intermediate compositions have a positive deviation from ideality and reflect local heterogeneities in the Na-Li disordered samples. Recent single-crystal X-ray work shows that,

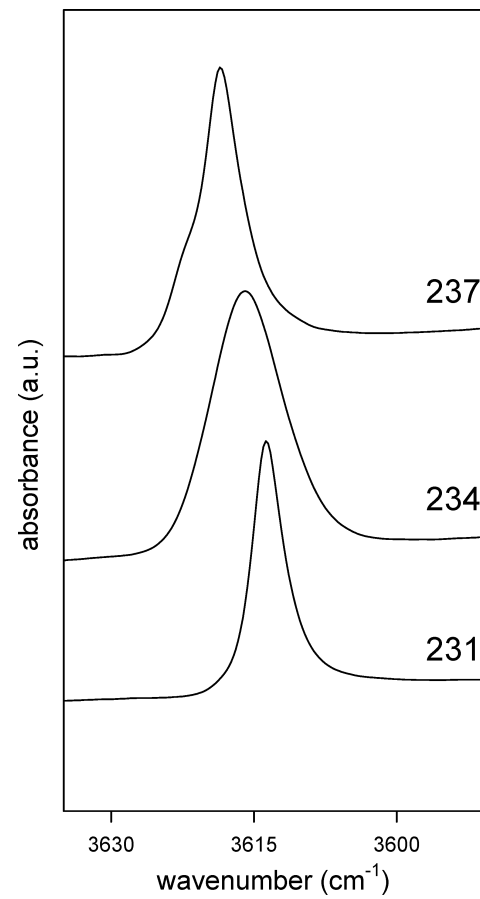

FIGURE 6. Enlargement in the 3630–3600 cm^{-1} region for selected amphiboles along the ferri-clinoferroholmquistite-riebeckite join.

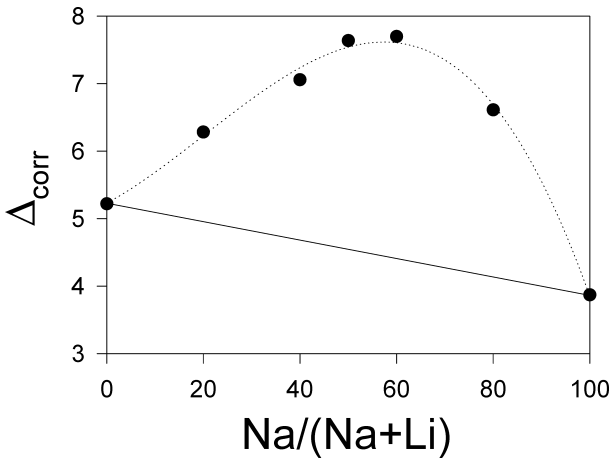

FIGURE 7. Variation in line width (Δ_{corr}) measured for the 3600–3625 cm^{-1} stretching region for synthetic amphiboles along the ferri-clinoferroholmquistite-riebeckite join.

in monoclinic amphiboles, Li occurs at a site (M4') closer to the strip of octahedra than that occupied by Na and Ca (M4), and adopts sixfold coordination (Oberti et al. 2003 and references therein). Therefore, local heterogeneities in intermediate Na-Li samples can be associated with the presence of two different B sites with slightly different geometries and distortions. The consequent slightly different charge contribution to O3 gives rise to slightly different O-H vibrational frequencies, which combine to give a broader absorption. The range in charge contribution can be quantified by the variation in the O-H band widths which gives the measure of the microscopic spontaneous strain induced by the distribution of Na and Li (and minor Fe^{2+}) at the B-site. As already observed by Carpenter and Boffa Ballaran (2001), Δ_{corr} can be compared directly to the enthalpy of mixing. Therefore, given the frequency range considered here (3600–3625 cm^{-1}), the characteristic length scale of phonons (which is known to scale with $1/\omega$, where ω = frequency: Salje 1992) must be of the order of magnitude of a single B site, i.e., ~4–5 Å.

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